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(54) IMPROVEMENTS IN OR RELATING TO OIL-SOLUBLE MIXED COPPER SOAP PRODUCTS

(71) We, TENNECO CHEMICALS INC., of 280 Park Avenue, New York 10017, United States of America, a corporation organised and existing under the laws of the State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

It is desirable for many purposes to be able to obtain dissolved copper-containing hydrocarbon oils. Such dissolved copper is generally obtained by dissolving or dispersing an oil-soluble copper soap in the hydrocarbon oil. Such dispersed copper is especially useful in fuel oils for removing or preventing the deposition of soot when burning the oil in furnaces or other equipment, such as locomotives and fire-up torches. Oil-soluble copper soaps are also useful as a source of soluble copper for use as catalysts in various liquid phase organic reactions, e.g. the preparation of adipic acid, and in the preparation of fungicides for use in oils or oil-miscible materials.

It has been recognized, heretofore, that various copper soaps are oil-soluble, including the copper soaps of the petroleum acids, i.e. the sulphonic acids, often referred to as the mahogany acids, and the naphthenic acids. These materials, however, are generally of a relatively high molecular weight so that in order to obtain a desired percentage, by weight, of copper dissolved in the oil, it was necessary to dissolve a relatively high percentage of the total soap in the oil.

Accordingly, it is desirable to use lower molecular weight copper soaps in order to obtain a higher proportion of copper dissolved for a given amount of soap added. Johnson, in U.S. Patent No. 2,622,671, describes copper soaps of certain lower molecular weight acids which are soluble in turpentine and which can then be dissolved in fuel oils. Johnson describes these as the salts of branched chain, acyclic, aliphatic carboxylic acids having from 5 to 12 carbon atoms, in which the carboxyl group is attached to a carbon atom other than the central carbon atom in the longest hydrocarbon chain. It has been found, however, that all such soaps are not generally soluble in nonpolar hydrocarbon solvents, such as mineral spirits; Johnson asserts that they are soluble in turpentine and then miscible with other materials. As these other nonpolar solvents are generally much less expensive to obtain or produce than turpentine and therefore, more likely to be commercially useful in such low cost, high volume uses as fuel oils, the need remains to obtain materials that provide a relatively high concentration of copper for as small a total amount of soap added as possible in an oil-miscible environment.

The present invention is directed to an oil-soluble mixed copper soap product comprising one or more soaps containing copper combined with acid groups derived from two structurally different organic monocarboxylic acids selected from saturated and olefinically unsaturated aliphatic carboxylic acids. This invention further provides a solution comprising a nonpolar hydrocarbon solvent or a halo-substituted nonpolar hydrocarbon solvent having dissolved therein the oil-soluble mixed copper soap composition as defined above.

The present invention includes an oil-soluble copper mixed soap comprising copper combined with two structurally different acid groups derived from the organic monocarboxylic acids defined above, and stable solutions of the copper mixed soaps in a nonpolar hydrocarbon solvent or chlorinated nonpolar hydrocarbon solvent.

This invention further includes a coprecipitated mixture of copper soaps of two structurally different carboxylic acids selected from saturated and olefinically unsaturated aliphatic monocarboxylic acids; a solution comprising a nonpolar hydrocarbon solvent or halo-substituted nonpolar hydrocarbon solvent containing dissolved therein a mixture of such salts is also a part of this invention.

The mixed copper soap product of this invention can broadly be prepared by the process comprising simultaneously reacting copper, in the form of combined or elemental copper, with acid group-containing compounds, there being present at least two structurally different acid groups, as defined above. It is, however, often not possible to determine the precise structure of the product according to this process, i.e. whether it is a copper mixed soap, a coprecipitated mixture of two normal soaps, or a coprecipitated combination or a mixed soap and two normal soaps. In such circumstances, defining the product in terms of the above preparation process is a complete definition of the product.

The mixed copper soap products of the present invention are in the form of a copper mixed soap or of the coprecipitated soap. The coprecipitated soaps can be prepared from a mixture of normal soaps, that are dissolved preferably from an intimate mixture, as by finely grinding together, and then removing the solvent.

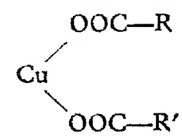
The term "normal soap" when used herein refers to the copper soap of a single acid, e.g. copper 2-ethylhexoate. The term "coprecipitated soaps" when used herein refers to a combination of two copper soaps obtained by removing the solvent from a solution of the two soaps or by causing the simultaneous precipitation of the two soaps from a solution of the two soaps.

In the preferred embodiments of this invention, the normal copper soaps of the acids used are insoluble but the mixed soap products of this invention are oil-soluble at room temperature in nonpolar oil miscible liquids, to form a solution stable at room temperature.

The copper mixed soap and coprecipitated copper soaps of this invention are generally more readily dissolved in oils and nonpolar hydrocarbon solvents and halo-substituted nonpolar hydrocarbon solvents tha nare mere mixtures of the normal copper soaps of the same acids. In addition, the solutions containing the dissolved copper soaps show a decreased viscosity when the mixed copper soap products are present as compared to the viscosity when only one of the normal copper soaps of the same acids is soluble and is dissolved in the same total proportions. There is also generally an improvement in the viscosity of the final solution compared to solutions obtained from normal copper soaps that are soluble. This decrease in viscosity results in an improved product which can be more readily handled and more easily mixed and otherwise processed.

It has been found that the isolated copper mixed soaps and coprecipitated soaps of the present invention behave differently from a mixture of the normal copper soaps of the same two structurally different acids. The copper mixed soaps and coprecipitated soaps of the present invention are not crystalline granular material as are the normal copper soaps of most of these acids, but rather, appear as a soft plastic mass, noncrystalline in appearance. A mechanical mixture of the copper soaps of the same acids does not dissolve in a nonpolar solvent as readily as the mixed soap in many instances. However many mixtures of soaps can usually be dissolved by heating, e.g. in mineral spirits, generally to form a stable solution. The coprecipitated soaps can, of course, then be obtained by evaporating off the solvent. Accordingly, mixed copper soap products of this invention include broadly all these types.

The copper mixed soaps of the present invention are believed to have the following structure:



wherein R and R′ are structurally different and selected from saturated aliphatic and olefinically unsaturated aliphatic groups. The R—COO and R′—COO groups are the residue of the corresponding monocarboxylic acids. In the so-called normal soaps, R and R′ are the same. The group of acids is subdivided into the following different structural groups. For example, the broad group: saturated aliphatic acids and olefinic acids, is sub-divided according to whether there is branching, and if so, the position of the branch closest to the carboxyl group: these include the straight-chain acids, e.g. normal octanoic acid or caprylic acid, the alpha-substituted branched-chain acids, e.g. 2 - ethylhexanoic acid, the beta-substituted branched-chain acids, e.g. 3,5,5 - trimethylhexanoic acid, the gamma-substituted branched-chain acids, e.g. 4 - ethyl - 5,5 - dimethylhexanoic acid and the delta-substituted branched-chain acids, e.g. 5 - ethyl - 6 - methylheptanoic acid. The position of, or even the existence of, further branching on the chain more than five carbon atoms removed from the carboxyl group has been found to have little or no effect in forming an oil-soluble mixed salt or a lower viscosity solution when mixed with a linear chain acid.

The alpha acids contain a first branched chain on the first carbon atom adjacent to the carboxyl group. The beta acids contain a first branched chain attached to the second carbon atom removed from the carboxyl group. In the gamma acids, the first branched chain is attached no closer than the third carbon atom from the carboxyl group.

Generally, the acid groups present in the mixed copper soap product or coprecipitated soaps of the present invention have at least

five carbon atoms in the molecule. Preferably, the acid groups will have from 20 carbon atoms, the upper limit not being a limit as to the effectiveness of the material in forming a soluble soap but rather as reaching a point where the proportion of copper in the molecule is so low as to render uneconomical the use of such a soap as a source of copper. The optimum acid groups contain from 6 to 11 carbon atoms.

Generally, the most useful compounds are the hydrocarbon acids because these are the most readily available at the lowest proces. However, the mixed copper soaps or coprecipitated soaps of this invention also include the soaps of acids which contain various inert substituent groups attached to the hydrocarbon chain or side chain. Such inert substituent groups include, particularly, the halogen atoms, especially chlorine, and oxygen atoms in the form of ether linkages along the chain of the carboxylic acid or in one of the branch chains.

Useful aliphatic acids are those having at least five carbon atoms and include the saturated linear fatty acids, such as valeric acid, caproic acid, caprylic acid (*n*-octanoic), pelargonic acid, *n*-decanoic acid, undecanoic acid and lauric acid. The alpha-branched saturated acids include 2-ethyl-butanoic acid, 2-ethyl-4-methylpentanoic acid, 2 - ethylhexanoic acid, 2,2,4,4 - tetramethylpentanoic acid, 2 - isopropyl - 2,3 - dimethylbutanoic acid, 2 - propyl - 4 - methylpentanoic acid, 2 - propylheptanoic acid, 2 - methylbutanoic acid, 2-methylpentanoic acid, 2,3 - dimethylpentanoic acid, 2,2 - dimethylpentanoic acid, 2 - ethyl - 3 - methylbutanoic acid, 2,5 - dimethylhexanoic acid, 2,2 - dimethylheptanoic acid, 2 - ethyl - 5 - methylhexanoic acid, 2 - methylnonanoic acid, 2 - ethyloctanoic acid, 2 - propylhexanoic acid and 2 - propyl - 5 - methylhexanoic acid. Beta branched acids include 3 - methylbutanoic acid, 3,3 - dimethylbutanoic acid, 3,3 - dimethylpentanoic acid, 3 - ethylpentanoic acid, 3,5 - dimethylhexanoic acid, 3 - ethyl - 4 - methylpentanoic acid, 3 - methyloctanoic acid, 3 - propylhexanoic acid, 3,5,5, - trimethylhexanoic acid and 3 - ethylnonanoic acid. The gamma and delta branched acids include 4 - methylpentanoic acid, 4 - methylhexanoic acid, 5 - methylhexanoic acid, 5 - methylheptanoic acid, 4 - ethyloctanoic acid, 4 - ethyl - 5,5 - dimethylhexanoic acid, 4 - methyldecanoic acid and 4,8 - dimethylnonanoic acid. Olefinically unsaturated monocarboxylic acids include 4 - pentenoic acid, 3-hexenoic acid, 2 - ethyl - 2 - hexenoic acid and 10 - undecenoic acid.

The presence or absence of unsaturation is not relevant to the structural difference. The presence and position, if present, of branching determines the structural difference, e.g. 10-undecenoic acid is structurally the same as *n*-nonanoic acid.

Generally, the saturated aliphatic monocarboxyclic acids are preferred for the practice of this invention as they are the most generally available and therefore, the most economical acids to be used in the preparation of soluble copper mixed salts.

The mixed copper soaps of the present invention can generally be prepared by reacting a source of copper, i.e. copper metal or a copper compound, including a salt or a hydroxide, with the desired organic acids or soluble salts of the acids, especially the sodium salts. The reactions are preferably carried out in a nonpolar, oil-miscible solvent so as to directly prepare the ultimately desired oil-miscible concentrated solution of copper. However, the reaction can also be carried out in an alcohol and/or water environment and the mixed soap separated as a solid before being dissolved.

The preparation from elemental copper can be carried out as follows: particulate, finely divided copper metal plus two structurally different organic acids, as defined above, are dispersed in a mineral spirits solvent together with water. The mixture is heated to from 60° to 90°C and is maintained at that temperature while it is agitated and air or oxygen is blown through the mixture as an oxidizing agent. The water is then distilled off after the reaction is complete, leaving the solution of the mixed copper salt in the mineral spirits solvent. The general reaction equation is as follows:

$$Cu + \tfrac{1}{2}O_2 + HA + HB \longrightarrow CuAB + H_2O,$$

wherein HA and HB are the structurally different acids.

A second method for preparing the copper mixed soap is by the reaction of cupric hydroxide with a mixture of the two organic carboxylic acids in a mineral spirits solvent to prepare a solution of the mixed copper salt. Sufficient amounts of the copper hydroxide and of the two acids are dispersed in the mineral spirits to produce the desired concentration of copper in the final solution and the reaction takes place at from 30° to 70°C. The reaction mixture is then heated to above the boiling point of the water formed. The final mineral spirits solution can then be used directly as a source of dissolved copper. The cupric hydroxide reagent which is used can also be a carbonated material having the formula ($CuCO_3 . Cu(OH)_2$).

The copper mixed salt can also be obtained from a double decomposition reaction, wherein cupric sulphate is reacted with a mixture of the sodium salts of the two desired acids in an aqueous system to form a mixture of the mixed

copper soap plus sodium sulphate. The sodium sulphate remains in solution in the water system whereas the copper mixed soap precipitates out and is thus readily separated.

Another procedure for preparing these materials is as follows: a saturated solution of copper acetate and hot water is treated with hot ethanol. Before a precipitate can form, a warm alcoholic solution of the two desired organic acids is added and the resulting solution kept warm for about 15 minutes. The mixed soap is then separated from the solvent by suitable means.

In each of the above precedures, the acid groups are preferably present in equimolar proportions; preferably the mixed acids are present slightly in excess of the amount of the copper present, preferably from 5 to 15 percent of molar excess. The presence of additional acid, of course, does not interfere with the reaction but is wasteful.

The acids can, if desired, be mixed in other than equimolar proportions; however, this will result in a product which is actually a mixture of the copper mixed soap plus the copper soap of whichever acid is present in excess. Such a mixture of the mixed soap plus additional copper salt has been found to be soluble for mixtures containing up to 200 percent molar excess of one of the acids. The excess amount of any acid that can be tolerated and still produce a soluble product is at least in part dependent upon the solubility of the salt of the acid present in excess in the mineral spirits or oil. Even the most insoluble acid salt can be present in excess to a certain degree, apparently through some sort of solubilizing effect of the mixed soap. Preferably, the maximum amount of excess is about 150 percent. Generally, even those acids that form the most insoluble salts of copper can be present up to about 50 percent in excess normal copper salt of that acid. The amount of the normal copper salt dissolved in the mineral spirits when formed from the excess acid can be above that which would be normally soluble in the nonpolar solvent, but it is soluble when present in solution with the mixed copper soap of the present invention.

In whatever form the copper and the structurally different acids are combined, i.e. as a true mixed salt, as a mixture of normal salts, or as a mixture of one or two normal salts and a mixed salt, the molar ratio of copper: Acid type A: Acid type B, is preferably 1:0.8—1.2:1.2—0.8. If there are more than two different acid groups present, but only two structural types of acids, e.g. *n*-octanoic, *n*-nonanoic and 2-ethylhexanoic acid, the acids of the same type are added together to determine the proportion of that type present. For example, 0.5 moles of *n*-octanoic acid, 0.6 moles of *n*-nonanoic acid and 1.1 moles of 2-ethylhexanoic acid give a ratio of acid type A: acid type B of 1:1.

The copper mixed soap of the present invention is believed to exist as a true compound and not merely as a solid solution of the two normal salts. Based upon the equilibrium distribution of the products from these chemical reactions, however, a mixture of the mixed salt plus proportions of the normal copper salts of each of the two acids is probably present. Accordingly, the "copper mixed soap" of the present invention can also be defined by the method in which it is prepared: a copper soap prepared by the simultaneous reaction with copper of the groups of two structurally different organic monocarboxylic acids, of the acids defined above. The coprecipitated copper salts which are also soluble in the proportions found for the mixed salts can be formed from the solutions of individually prepared normal salts that are mixed and then coprecipitated. Generally, when the normal copper salts of any one of the above defined acids are prepared by the methods described above in a mineral spirits solvent, an unstable solution is formed, from which the copper soap precipitates at varying times after cooling to room temperature. If the solutions were mixed before precipitation, a stable solution is formed; especially where the copper soaps are present in equimolar amounts, or within the range of excess described above for the mixed salt. When the solvent is removed to form a coprecipitate, the coprecipitate can be redissolved to form a stable solution.

Also, generally, the mixed soaps or coprecipitated soaps, can be prepared by any method used for the preparation of the normal copper soaps, merely substituting a mixture of two structurally different acids, preferably in about an equimolar mixture, as explained above, to form the desired mixed acid soap. For such normal soap preparations see, for example, U.S. Patent Nos. 2,584,041 and 2,113,496.

Generally, the alpha-branched saturated aliphatic carboxylic acids and the straight chain aliphatic acids provided salts of copper having the lowest solubility. The beta- and the gamma-branched acids have somewhat higher solubilities in mineral spirits or other nonpolar hydrocarbon solvents; therefore, the alpha-branched and straight chain acids should not be tolerated in as great an excess before precipitation would occur from an oil solution as the more soluble salts of the beta or gamma acids. Further, the copper salts of the branched chain acids having a quaternary carbon atom at the terminal point of the chain furthest away from the carboxyl group tend to be as insoluble as the salts of the alpha acids. A surprising aspect of the present invention is that the mixed salts formed from mixtures of alpha-

branched and straight chain saturated aliphatic acids are substantially as soluble as are the mixed salts formed from an alpha-branched and a beta-branched acid or the mixed salt of a beta and a gamma acid, etc.

The oil-soluble mixed copper soap of the present invention is soluble in a nonpolar hydrocarbon solvent or a halogenated nonpolar hydrocarbon solvent. The hydrocarbon solvents include the liquid distillates, or mineral spirits (hydrocarbon distillates), such as gasoline, kerosene, the diesel fuels 1, 2, and 3, the higher-boiling distillates, known as fuel oils 4, 5 and 6, as well as aromatic hydrocarbon oils. In addition, the mixed soaps are soluble in fuels which become liquid only when preheated, such as higher melting residual oils which are semi-solid in nature and must be heated to temperature of the order of 180°F. to increase their fluidity before they may be used as burning fuels of the liquid type. Other non-petroleum derivative solvents for the oil-soluble mixed copper soaps include xylene, turpentine, toluene and ethyl benzene.

Useful chlorinated organic solvents include *o*-dichlorobenzene, carbon tetrachloride, ethylene dichloride and perchloroethylene.

As stated above, the use of a halogenated e.g. chlorinated, acid is contemplated in the preparation of the mixed soap. The halogenated acids are not at present sufficiently low in cost as to be economically useful as an additive for a fuel oil. If in the future such chlorinated acids do become cheaply available or if, in specific instances, there are such halogenated acids available as a side product or by-product from other reactions, they can be usefully used to improve the effectiveness of the soot remover composition in accordance with the suggestion of Johnson in U.S. Patent No. 2,622,671. Chlorinated organic compounds, generally, can provide a source of chlorine in the concentrate. The chlorine reacts with copper to reduce soot formation apparently by lowering the ignition temperature of the soot deposits. Johnson suggests adding a separate chlorinated organic compound. However, where chlorinated acids are available, one of these could be used to form the mixed soap with another structurally different organic acid, or halogenated acid, in lieu of a mixture of the soap plus a separate chlorinated hydrocarbon compound.

The following Examples represent certain preferred embodiments of the present invention and the preparation of certain of the mixed soaps and mineral spirits concentrates containing the mixed soap dissolved therein.

The coprecipitated mixture of copper salts of two structurally different saturated or olefinically unsaturated monocarboxylic aliphatic acids is sufficiently soluble in mineral spirits to form a solution containing 6% by weight of copper. The stable solution comprising a nonpolar hydrocarbon solvent or a chlorinated nonpolar hydrocarbon salt and an oil-soluble mixed copper soap product contains at least 6% by weight of dissolved copper. Furthermore, the stable solution comprising a nonpolar hydrocarbon solvent or a chlorinated non-polar hydrocarbon solvent and combined copper and acid groups derived from two structurally different saturated or olefinically unsaturated monocarboxylic aliphatic acids is capable of being concentrated to a percent by weight of copper of at least 6% without the precipitation of copper.

Comparative Examples A—M

A series of normal copper soaps were prepared by the following procedure, using 2,2-dimethylpentanoic acid as an example:

The acid (136g), mineral spirits (230g) and cupric hydroxide (49g) were charged to a flask at room temperature, heated, with mechanical agitation, to 75°—80°C and then maintained at that temperature until all of the cupric hydroxide had dissolved. The mixture was then heated to 120°C to eliminate the water formed. Where there was no immediate precipitation, the solution was diluted with mineral spirits to about 8 percent by weight copper (to about 398g total weight of solution) and filtered while hot (100°—110°C.) to remove any unreacted copper hydroxide. These procedures were carried out with about 4 percent excess acid, which tends to promote solubility.

The appearance of the soap product obtained from each acid used is set out in Table I, below. In each case, the same amount of copper hydroxide was used (49g):

TABLE I

Normal Copper Soaps

Comparative Example	Acid Group	Grams of Acid Used	Grams of Mineral Spirits Used	Solubility of Soap in Mineral Spirits Solvent
A	2,2-Dimethylpentanoic	136	230	Partially soluble in mineral spirits at room temperature (up to 2%, by wt. copper)
B	2-Ethyl-4-methylpentanoic	150	216	Crystallized 100°—120°C.
C	2-Ethylhexanoic	150	216	Crystallized 95°—105°C.
D	2-Propyl-4-methylpentanoic	165	201	Crystallized at 110°—120°C.
E	2-Propylheptanoic	180	186	Crystallized upon cooilng to room temperature
F	2-Ethyl-2-Hexanoic	150	216	Crystallized at 100°—120°C.
G	3,5,5-Trimethylhexanoic	165	201	Crystallized slowly upon aging at room temperature after 3 days
H	4-Ethyl-5,5-dimethylhexanoic	180	186	Solidified completely at room temperature
I	4-Methyl pentanoic	121	245	Crystallized upon cooling at room temperature
J	*n*-Octanoic	150	216	Solidified completely at room temperature
K	*n*-Nonanoic	165	201	Solidified completely at room temperature
L	10-Undecenoic	194	172	Solidified completely at room temperature
M	*n*-Hexanoic	121	245	Substantially all crystallized at room temperature

As shown by the results set out in Table I, none of the normal soaps of copper are sufficiently oil-soluble to provide a stable solution in mineral spirits of 8 percent copper, and only one is soluble to more than 1 percent copper. Four of the soaps solidified completely, forming a gel in the mineral spirits solvent.

Example 1.

A stable solution of an oil-soluble copper mixed soap was obtained by mixing 1.07 g-mols 2 - ethylhexanoic acid, 1.07 g-mols 3,5,5 - trimethylhexanoic acid and 1.0 mol copper hydroxide ($Cu(OH)_2$) in mineral spirits. The materials were mixed and heated to from 30° to 70° C. until the reaction was substantially completed. The solution was then heated to 120° C. to eliminate the water formed during the reaction, filtered to remove any unreacted copper hydroxide and then diluted with sufficient additional mineral spirits to produce a solution containing 8 percent by weight of copper of the mixed copper carboxylates.

The clear solution was then concentrated by distillation to 10 percent by weight copper; the viscosity of this solution was determined to be E(1.25 stokes) of the Gardner-Holdt scale. The mineral spirits used in this preparation had the following composition: 6.7% aromatics, 91.3% saturates and 2% olefins (Shell (Registered Trade Mark) Mineral Spirits 145—66).

The solvent was then distilled off and the solid mixed copper soap was obtained. The solid mixed soap was of a soft plastic consistency and was coloured green. The mixed soap was then completely redissolved at room temperature in additional mineral spirits to prepare a stable solution containing 8 percent copper.

Example 2.

The procedure of Example 1 was repeated several times but in each case using different proportions of the 2-ethylhexanoic acid (alpha acid) and 3,5,5-trimethylhexanoic acid (beta acid). The solution of the mixed soap in the mineral spirits solvent was permitted to cool by standing, and the following results were observed:

Molar Ratio of Alpha Acid to Alpha Plus Beta Acids	Observations
0.388	Considerable dark green granular material
0.5	Stable solution
0.612	Stable solution
0.756	Some dark green material deposited

Example 3.

The mixed soap of copper 2 - ethylhexanoate/3,5,5 - trimethylhexanoate was prepared as follows: 50 g of finely divided copper metal (98% through a #325 mesh screen) was mixed with 118 g of 2 - ethylhexanoic acid and 129.5 g of 3,5,5 - trimethylhexanoic acid, dispersed in the mineral spirits solvent as used in Example 1 in a 3-necked one-litre round bottom flask fitted with a reflux condenser, propeller agitator and fritted glass air injection tube extending to the bottom of the flask. The copper and the acids were dispersed in the mineral spirits and the dispersion was then heated to 80° C. Water (25 g) was then added to the mixture and air blown through the mixture while it was vigorously agitated. After the reaction had gone to completion, any remaining solid material was filtered out. The solution was vacuum distilled at 100° C. and a pressure of 25 mmHg absolute to remove any remaining water.

The mineral spirits solvent was evaporated to obtain the mixed soap of copper 2 - ethylhexanoate/3,5,5 - trimethylhexanoate. The solution was diluted with mineral spirits to a concentration of 10 percent copper, to form a dark green solution having the same properties as that obtained in Example 1. This material readily dissolves in the mineral spirits to form the desired 8 percent by weight copper solution.

Example 4.

The mixed soap of 2 - ethylhexanoic acid and 3,5,5 - trimethylhexanoic acid is also formed by the reaction of 1 mol of cupric sulphate mixed with 1.07 mols each of sodium 2 - ethylhexanoate and sodium 3,5,5 - trimethylhexanoate. The sodium salts are dissolved in water and heated to 70° C. The mixed soap of copper 2 - ethylhexanoate/3,5,5 - trimethylhexanoate precipitates out and is readily separated as a soft plastic mass identical to that formed in Example 1. The solid material is dried and then readily dissolves in the mineral spirits as used in Example 1 to form a stable solution.

Example 5.

1 g-mol of copper acetate is dissolved in hot water to form a saturated solution. To this

saturated solution is added 200 mls of hot ethanol at 70° C. Immediately thereafter, and before a precipitate could form, a solution in alcohol of 1.11 g-mols each of 2 - ethylhexanoic acid and 3,5,5 - trimethylhexanoic acid is added to the copper acetate solution which is maintained at 70°C for about 15 minutes. The alcohol and water mixture is heated away to leave the mixed copper salt.

Example 6.

The procedure of Example 1 was followed with 2 - ethyl - 4 - methylpentanoic acid being substituted for the 2 - ethylhexanoic acid. The mixed copper soap of the two acids was obtained as a green plastic deposit, which readily redissolved in mineral spirits to form an 8 percent copper stable solution.

Examples 7—17.

The procedure of Example 1 was followed but using the acids and the proportions set forth in Table II, below. In each case, 49 g of copper hydroxide was used and a stable solution containing 8 percent by weight of copper was prepared.

TABLE II

Acids Used	Acid (A) (g)	(B) (g)	Min Spirits (g)	Grams of 8% Copper Solution Obtained	Yield (%)
A) 2,2-Dimethyl pentanoic B) 3,5,5-Trimethyl hexanoic acid	68	82.5	215.5	382	96.0
A) 2-Ethyl-4-methyl pentanoic B) 3,5,5-Trimethyl hexanoic acid	75	82.5	208.5	385	96.8
A) 4-Ethyl-5,5-dimethyl hexanoic B) 3,5,5-Trimethyl hexanoic acid	90	82.5	193.5	393	98.8
A) *n*-Nonanoic B) 3,5,5-Trimethyl hexanoic acid	82.5	82.5	201	395	99.2
A) 10-Undecenoic B) 3,5,5-Trimethyl hexanoic acid	97	82.5	186.5	377	94.8
A) 2-Ethyl-2-hexanoic B) 3,5,5-Trimethyl hexanoic acid	75	82.5	208.5	Thick, but clear solution obtained	Not determined estimated over 90%
A) 4-Ethyl-5,5-dimethyl hexanoic B) 2-Ethyl hexanoic acid	90	75	201	395	99.2
A) *n*-Nonanoic B) 2-Ethyl hexanoic acid	82.5	75	208.5	392	98.5
A) 4-Methyl pentanoic B) *n*-Hexanoic	60.5	60.5	245	382	96.0
A) 4-Methyl pentanoic B) 3,5,5-Trimethyl hexanoic acid	60.5	82.5	223	381	95.7
A) 2-Ethyl butanoic B) 3,5,5-Trimethylhexanoic acid	60.5	82.5	233	381	95.7

The above Examples all show that the copper mixed soaps of organic carboxylic acids which do not form copper soaps that are normally soluble at room temperature or that do not form stable solutions in mineral spirits, surprisingly are oil-soluble and form stable solutions in mineral spirits at room temperature. However, when a mixed soap formed from a mixture of two acids of the same structural type, as defined above, are used, the mixed soap is not soluble.

Comparative Example N.

The procedure in Example 1 was repeated but substituting for the two acids used 2-ethylhexanoic acid and the mixed alpha acids known as "Versatic" (Regd. Trade Mark) 9 (56% 2,2,4,4 - tetramethylpentanoic acid and 27% 2 - isopropyl - 2,3 - dimethylbutanoic acid). The material did not form a stable solution but immediately precipitated out as a dark green, granular copper soap. The precipitation occurred at elevated temperatures of about 95° to 100°C, even before the solution could cool.

Comparative Example O.

The procedure of Example 1 was repeated but substituting caprylic acid and pelargonic acid for the two acids used. The product formed precipitated out as the dark green copper soaps of caprylic and pelargonic acids immediately upon cooling to room temperature. These materials could not be redissolved in a mineral spirits solution.

Comparative Examples P—R.

The procedure of Example 1 was repeated, but substituting the acid pairs and amounts set forth in Table III. Each pair of acids in Examples P—R respectively are in the same structural group. The results obtained were as follows:

TABLE III

Acid Pairs	Grams Acid Used	Grams Min. Spirits Used	Solubility of mixed soap in mineral spirits solvent
2-Ethyl hexanoic 2-Ethyl-4-methyl pentanoic	75 75	216	Crystallized at 100°—110°C
2-Ethyl hexanoic 2-Ethyl-2-hexanoic	75 75	216	Crystallized at 100°—110°C
2-Ethyl hexanoic 2,2-Dimethyl pentanoic	75 68	223	Crystallized partially at 100°—110°C; more upon cooling to room temperature

As shown, by each of Examples N—R, mixed soaps formed from two acids that are structurally the same are not oil-soluble where the normal copper soap of each acid is insoluble in the mineral spirits solvent.

Example 18.

A freshly-prepared solution of copper 3,5,5-trimethyl hexanoate in mineral spirits as prepared in Comparative Example G (398 g, 8% copper) was maintained at 100°C and mixed with a solidified copper 4 - ethyl - 5,5 - dimethyl hexanoate solution (398 g, 8% copper) as prepared in Comparative Example H. The mixture was heated to 120°C to form a uniform solution and held there for 5—10 minutes. The temperature was cooled to room temperature and the solution remained clear and stable.

A coprecipitate can be obtained by evaporating off the mineral spirits solvent. The coprecipitate can be readily redissolved in mineral spirits at room temperature.

Examples 19 and 20.

The procedure of Example 18 was repeated but substituting the salts in accordance with Table IV below. The mixture is dissolved at the temperature indicated in Table IV to form a stable solution in each case.

TABLE IV

Example	Salt A and (Condition)	Salt B and (Condition)	Dissolution Temperature	Condition on Cooling To Room Temperature
19	Copper 3,5,5-Trimethyl hexanoate (Solution) (Example G)	Copper-Nonanoate (Solidified Solution) (Example K)	80°C	Clear and Stable Solution
20	Same as (19)	Copper Caprylate/n-Nonanoate (solidified solution) (Example 0)	74°C	Clear and Stable Solution

Both Examples 19 and 20 formed solutions of the mixed salts that were clear and stable. They could be evaporated to form a coprecipitated mixture of salts that could be redissolved in the mineral spirits solvent.

Example 21.

A stable, clear solution in *o*-dichlorobenzene of an oil-soluble mixed copper soap product was obtained by mixing 1.07 g-mols 2,2 - dimethylpentanoic acid, 1.07 g-mols 3,5,5 - trimethylhexanoic acid and 1.0 mols copper hydroxide ($Cu(OH)_2$) in *o*-dichlorobenzene. The materials were mixed and heated to form 30° to 70°C until the reaction was substantially completed. The solution was next heated to 120°C to eliminate any water formed during the reaction and then diluted with sufficient additional *o*-dichlorobenzene to produce a clear green solution of the mixed copper soaps containing 8 percent by weight of copper.

Example 22.

The procedure of Example 21 was repeated substituting xylene for the *o*-dichlorobenzene. After preparing the solution, the xylene can be readily boiled away and the solid mixed copper soap obtained. The mixed soap was coloured green and had a soft plastic consistency. The mixed soap was then readily redissolved in xylene at room temperature to prepare a stable solution containing 8 percent copper.

The concentrated mineral spirit solutions of the mixed copper soaps prepared above are suitable for directly mixing with a fuel oil or other hydrocarbon fuel to add the desired amount of the soluble copper as a soot remover additive. Generally, a concentrated solution containing 8 percent by weight of the copper metal is added in a one part per thousand ratio to fuel oil; higher molecular weight, i.e. higher boiling point fuel oils, and the semi-solid so-called "residual" oils that generally have a higher carbon content will require a somewhat higher percentage or proportion of the concentrate, perhaps from 1 part per 200 to 800 parts of the fuel oil. Broadly, the concentrated solution is preferably added in a proportion of 1 part to from 200 to 2000 parts of fuel oil.

WHAT WE CLAIM IS:—

1. An oil-soluble copper mixed soap of two structurally different saturated or olefinically unsaturated aliphatic monocarboxylic acids.

2. An oil-soluble mixed copper soap product comprising copper combined with acid groups derived from two structurally different saturated or olefinically unsaturated aliphatic monocarboxylic acids.

3. A soap product according to claim 2, wherein the aliphatic acids are straight chain acids, alpha-substituted branched chain acids, beta-substituted branched chain acids, gamma-substituted branched chain acids or delta-substituted branched chain acids.

4. A soap product according to claim 2 or 3, wherein the acids each contain at least five carbon atoms.

5. A soap product according to claim 4, wherein the acids each contain from five to twenty carbon atoms.

6. A soap product according to claim 4, wherein the acids each contain from six to eleven carbon atoms.

7. A soap product according to any of claims 2 to 6, wherein at least one acid is a saturated acid.

8. A soap product according to claim 7, wherein the or each saturated acid is an alpha or a beta-substituted branched chain acid or a straight chain acid.

9. A soap product according to claim 8, wherein the acids comprise one alpha-branched and one beta-branched saturated acid.

10. A soap product according to any of claims 2 to 6, wherein the acids comprise at least one olefinically unsaturated acid.

11. A soap product according to claim 10, wherein the or each olefinically unsaturated acid is an alpha or beta-substituted branched chain acid or a straight chain acid.

12. A soap product according to any of claims 2 to 9, wherein the acids are 2-ethylhexanoic acid and 3,5,5-trimethylhexanoic acid.

13. A soluble mixed copper soap product according to claim 2, substantially as hereinbefore described with reference to Examples 1 to 17.

14. A process of preparing an oil-soluble mixed copper soap product comprising simultaneously reacting copper, in the form of either combined or elemental copper, with acid group-containing compounds containing two structurally different saturated or olefinically unsaturated aliphatic monocarboxylic acid groups.

15. A process according to claim 14, wherein the acid group-containing compounds are the acids or the salts of the acids.

16. A process according to claim 14 or 15, wherein the copper is in the form of hydroxide.

17. A process according to claim 14 or 15, wherein the copper is in the form of metal.

18. A process according to claim 14 or 15, wherein the copper is in the form of acetate.

19. A process according to claim 14 or 15, wherein the copper is in the form of a water-soluble salt and the acids are in the form of aqueous solutions of sodium salts.

20. A process according to claim 19, wherein the copper salt is copper sulphate.

21. A process according to any of claims 14 to 20, wherein the mol ratio of a first acid to a structurally different acid is from 2:1 to 1:2.

22. A process of preparing an oil-soluble

mixed copper soap product according to claim 14, substantially as hereinbefore described with reference to Examples 1 to 17.

23. An oil-soluble coprecipitated mixture of copper soaps of two structurally different saturated or olefinically unsaturated monocarboxylic aliphatic acids, the coprecipitated mixture being sufficiently soluble in mineral spirits to form a solution containing 6% by weight of copper.

24. A coprecipitated mixture according to claim 22, wherein the mol ratio of one structurally different acid group to a second structurally different acid group is from 2:1 to 1:2.

25. An oil-soluble coprecipitated mixture according to claim 23, substantially as hereinbefore described with reference to Examples 18 to 20.

26. A stable solution containing at least 6% by weight of dissolved copper comprising a nonpolar hydrocarbon solvent or a chlorinated nonpolar hydrocarbon solvent and an oil-soluble mixed copper soap product according to claim 2.

27. A stable solution comprising a nonpolar hydrocarbon solvent or a chlorinated nonpolar hydrocarbon solvent, combined copper and acid groups derived from two structurally different saturated or olefinically unsaturated monocarboxylic aliphatic acids, the solution being capable of being concentrated to a percent by weight of copper of at least 6% without the precipitation of copper.

28. A stable solution according to claim 27, wherein the polar proportion of one acid group to a second structurally different acid group is from 2:1 to 1:2.

29. A stable solution according to claim 27, substantially as hereinbefore described with reference to Examples 21 and 22.

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